

CHEMICAL KINETICS

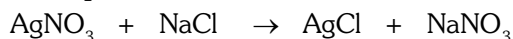
2.0 INTRODUCTION

Chemical Kinetics is the branch of physical chemistry which deals with the study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.

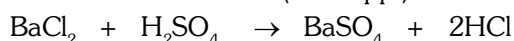
On the basis of rate, chemical reaction are broadly divided into three categories :-

(a) Very fast or instantaneous reactions : Generally these reactions involve ionic species and known as ionic reactions. These reactions take about 10^{-14} or 10^{-16} seconds for completion. So, it is almost impossible to determine the rate of these reactions.

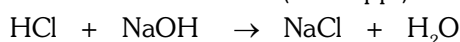
Examples :



(white ppt)



(white ppt)

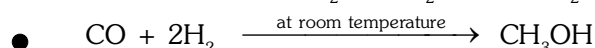


(b) Very slow reactions : These reactions proceed very slowly, may take days or months to show any measurable change at room temperature.

Examples :

- Rusting of iron.

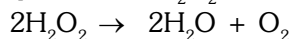
- Reaction between H_2 and O_2 to form H_2O at ordinary temperature in absence of catalyst.



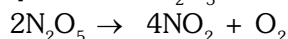
(c) Moderate or slow reactions : This type of reactions proceed with a measurable rates at normal temperature and we can measure the rate of these reactions easily. Mostly these reactions are molecular in nature.

Examples :

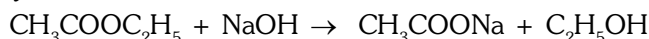
- Decomposition of H_2O_2



- Decomposition of N_2O_5

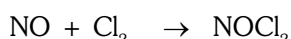


- Hydrolysis of ester



- Inversion of cane sugar in aqueous solution

- Reaction of NO with chlorine



2.1 RATE OF REACTION

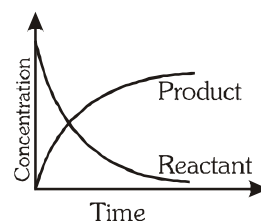
Rate of reaction is defined as the change in concentration or pressure of reactant or product per unit time. It is always a positive quantity.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken in change}} \quad \boxed{r = \pm \frac{\Delta C}{\Delta t}}$$

Where ΔC = change in concentration in a small interval Δt
[+] sign is used when we refer for product concentration.
[-] sign is used when we refer for reactant concentration.

For gaseous reactions $r = \pm \frac{\Delta P}{\Delta t}$ (unit of rate = pressure time⁻¹)

$$\text{and } r = \frac{1}{RT} \times \left[\pm \frac{\Delta P}{\Delta t} \right] \quad (\text{unit of rate} = \text{M time}^{-1})$$



Types of Rate of Reactions :-

(A) Average Rate of Reaction

The rate of reaction over a certain measurable period of time during the course of reaction is called average rate of reaction. It is denoted by \bar{r} .

For a reaction $A \longrightarrow B$

$$r_{\text{average}} = \bar{r} = \left(\frac{[A]_2 - [A]_1}{t_2 - t_1} \right) = - \frac{\Delta[A]}{\Delta t}$$

Where $[A]_1$ = Concentration of reactant A at time t_1 ,

$[A]_2$ = Concentration of reactant A at time t_2 .

(B) Instantaneous Rate of Reaction

The rate of reaction at any particular instant during the course of reaction is called instantaneous rate of reaction.

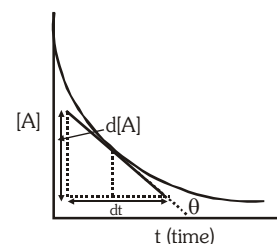
For a reaction $A \longrightarrow B$

Mathematically ; Instantaneous rate = $\lim_{\Delta t \rightarrow 0}$ (Average rate)

$$r_{\text{inst}} = \lim_{\Delta t \rightarrow 0} \left(- \frac{\Delta[A]}{\Delta t} \right) = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta[B]}{\Delta t} \right) \quad \text{or} \quad \boxed{r_{\text{inst}} = (-) \frac{d[A]}{dt} = (+) \frac{d[B]}{dt}}$$

Hence, Slope of the tangent at time t in plot of concentration with time gives instantaneous rate of reaction.

$$\text{Instantaneous rate of reaction} = \lim_{\Delta t \rightarrow 0} \left(\pm \frac{\Delta C}{\Delta t} \right) = \pm \frac{dC}{dt}$$



2.2 RATE OF REACTION IN THE FORM OF STOICHIOMETRY OF A CHEMICAL REACTION

Let us consider a reaction : $m_1A + m_2B \rightarrow n_1P + n_2Q$

Where, Rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of appearance of P = $\frac{d[P]}{dt}$

Rate of appearance of Q = $\frac{d[Q]}{dt}$

$$\boxed{\text{Rate of reaction} = \frac{1}{m_1} \left(- \frac{d[A]}{dt} \right) = \frac{1}{m_2} \left(- \frac{d[B]}{dt} \right) = \frac{1}{n_1} \frac{d[P]}{dt} = \frac{1}{n_2} \frac{d[Q]}{dt}}$$

- Rate of reaction is always positive; negative sign represents decrease in concentration of reactant.

Units of Rate of Reaction

Unit of rate of reaction = $\text{mol L}^{-1} \text{time}^{-1}$ i.e. ($\text{mol L}^{-1} \text{s}^{-1}$ or $\text{mol L}^{-1} \text{min}^{-1}$ or $\text{mol L}^{-1} \text{h}^{-1}$)



Illustrations

Illustration 1. For the reaction : $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. If the concentration of NO_2 increases by $1.6 \times 10^{-2} \text{ M}$ in 4 s. Calculate the following -

- (i) rate of formation of NO₂
 (ii) rate of formation of O₂
 (iii) rate of disappearance of N₂O₅
 (iv) rate of reaction

Solution.

(i) Rate of formation of NO_2 : $\frac{d[\text{NO}_2]}{dt} = \frac{1.6 \times 10^{-2}}{4} = 4.0 \times 10^{-3} \text{ M/s}$

(ii) Rate of formation of O_2 : $\frac{d[\text{O}_2]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{1}{4} \times 4 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$

(iii) Rate of disappearance of N_2O_5 : $\frac{-d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \times 4 \times 10^{-3} = 2.0 \times 10^{-3} \text{ M/s}$

$$\text{(iv) Rate of reaction} = \frac{1}{2} \left(-\frac{d[\text{N}_2\text{O}_5]}{dt} \right) = \frac{1}{2} \times 2 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$$

$$\text{or } \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{1}{4} \times 4 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M/s}$$

$$\text{or } \frac{d[\text{O}_2]}{dt} = 1.0 \times 10^{-3} \text{ M/s}$$

Illustration 2. Express the rate of reaction for the following changes :

- (a) $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$
(b) $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

Solution.

(a) Rate of reaction $= \frac{1}{2} \left(-\frac{d[\text{HI}]}{dt} \right) = \frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt}$

$$(b) \text{ Rate of reaction} = \frac{1}{2} \left(-\frac{d[\text{SO}_2]}{dt} \right) = \frac{-d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

BEGINNER'S BOX-1

1. The rate of a reaction is expressed as :

$$+\frac{1}{2}\frac{\Delta[C]}{\Delta t}=\frac{1}{3}\frac{\Delta[D]}{\Delta t}=\frac{1}{4}\left(-\frac{\Delta[A]}{\Delta t}\right)=\left(-\frac{\Delta[B]}{\Delta t}\right)$$

Then reaction is

- (1) $4A + B \rightarrow 2C + 3D$
(3) $A + B \rightarrow C + D$

- $$\begin{aligned} (2) \quad & \text{B} + 3\text{D} \rightarrow 4\text{A} + 2\text{C} \\ (4) \quad & \text{B} + \text{D} \rightarrow \text{A} + \text{C} \end{aligned}$$

2. In the reaction, $A + 2B \rightarrow 6C + 2D$ if the initial rate $(-)\frac{\Delta[A]}{\Delta t}$ at $t = 0$ is $2.6 \times 10^{-2} \text{ M s}^{-1}$, what will

be the value of $(-)\frac{\Delta[B]}{\Delta t}$ at $t = 0$?

- (1) $8.5 \times 10^{-2} \text{ M s}^{-1}$ (2) $2.6 \times 10^{-2} \text{ M s}^{-1}$ (3) $5.2 \times 10^{-2} \text{ M s}^{-1}$ (4) $7.5 \times 10^{-2} \text{ M s}^{-1}$

3. In the following reaction, how is the rate of appearance of the underlined product related to the rate of disappearance of the underlined reactant $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\ell) + 3\text{H}_2\text{O}(\text{aq})$

(1) $(-)\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$ (2) $(-)\frac{1}{3}\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{\Delta[\text{Br}_2]}{\Delta t}$ (3) $(-)\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = \frac{1}{3}\frac{\Delta[\text{Br}_2]}{\Delta t}$ (4) None of these



2.3 RATE LAW

The experimental expression of rate of reaction in terms of concentration of reactants is known as rate law. In this expression the rate of a reaction is proportional to the product of molar concentration of reactants with each term raised to the power or exponent that has to be found experimentally.

In a chemical reaction :- $aA + bB \longrightarrow \text{Product}$

The rate law is :- $\text{Rate} \propto [A]^x[B]^y$

The values of exponents x and y are found experimentally which may or may not be same as stoichiometric coefficients.

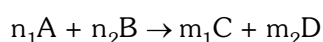
Above relationship can be written as :-

$$\text{Rate} = k[A]^x[B]^y$$

Where k is a proportionality constant known as rate constant.

Rate constant :

In a chemical reaction –



according to law of mass action

$$\text{Rate} = k[A]^{n_1}[B]^{n_2}$$

but according to rate law (experimental concept)

$$\text{Rate} = k[A]^x[B]^y$$

if $[A] = [B] = 1 \text{ mol/L}$

then, $\text{Rate} = k$

Rate of reaction at unit concentration of reactants is called as rate constant or specific reaction rate.

Rate constant does not depend on concentration of reactant but it depends on temperature and catalyst.

2.4 ORDER OF REACTION –

The sum of powers of concentration of reactants in rate law expression is known as order of reaction.

For the reaction $aA + bB \rightarrow \text{Product}$

Rate law is $\text{Rate} = k[A]^x[B]^y$

Here $x = \text{order of reaction with respect to A}$

$y = \text{order of reaction with respect to B}$

$x + y = n$ (overall order of reaction)

- Order of reaction may be zero, positive, negative or fractional.
- Order of reaction is an experimental quantity.

Units of rate constant :

$$\text{Rate} = k[A]^n$$

$$k = \frac{r}{[A]^n} = \frac{\text{unit of rate}}{[\text{unit of concentration}]^n} = \frac{\frac{\text{mol}}{\text{L}} \times \text{time}^{-1}}{\left[\frac{\text{mol}}{\text{L}}\right]^n}$$

- Unit of $k = \left[\frac{\text{mol}}{\text{L}}\right]^{1-n} \times \text{time}^{-1}$
- For gaseous reaction unit of k may be $= (\text{atm})^{1-n} \times \text{time}^{-1}$



2.5 MECHANISM OF REACTION :

(a) Elementary reactions :

Those reactions which completes in single step and which have exponents in rate law equal to stoichiometric coefficients of the reactants.

If $A + B \longrightarrow \text{Products}$; is an elementary reaction

then rate law will be –

$$\text{Rate} = k[A][B]$$

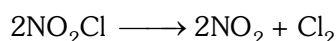
- Zero order reactions can never be elementary reactions.
- For elementary reactions fractional order is not possible.

(b) Complex reactions :

Those reactions which complete in multisteps. For these reactions a mechanism is proposed.

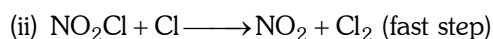
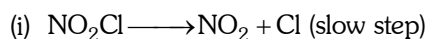
- For complex reactions the overall rate of reaction is controlled by the slowest step which is called as rate determining step (R.D.S.).
- In rate law expression rate of reaction depends on concentration of reactants of slowest step which must be free from intermediate.
- If R.D.S. contains intermediate, its value is solved using K_{eq} of fast step (assumed as reversible)

Example-1



Experimentally, the rate law is $\text{Rate} = k[\text{NO}_2\text{Cl}]$

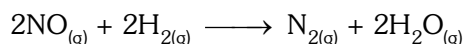
The mechanism of the reaction is given as –



So the rate law from slowest step $\text{Rate} = k[\text{NO}_2\text{Cl}]$

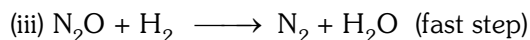
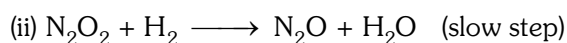
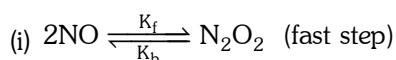
In this way the predicted rate law derived from two step mechanism agrees with experimental rate law.

Example-2



experimentally the rate law is, $\text{Rate} = k [\text{NO}]^2[\text{H}_2]$

The mechanism of the reaction is given as –



The Rate law from slowest step is :

$$\text{Rate} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

The rate law expression should be free from intermediate species N_2O_2 .

From fast reversible step –

$$k_f[\text{NO}]^2 = k_b[\text{N}_2\text{O}_2]$$

$$\therefore [\text{N}_2\text{O}_2] = \frac{k_f}{k_b} [\text{NO}]^2$$

and rate law becomes

$$\text{Rate} = k \left(\frac{k_f}{k_b} \right) [\text{NO}]^2 [\text{H}_2]$$

therefore, $\text{Rate} = k'[\text{NO}]^2[\text{H}_2]$

This derived rate law agrees with experimental rate law.



2.6 MOLECULARITY

Total number of molecules, atoms or ions (reacting species) participating in an elementary reaction is called as molecularity of reaction.

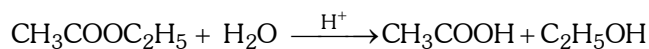
- Molecularity is a theoretical quantity.
- Molecularity can be an integer (1, 2 or 3) but it cannot be zero or negative or fractional.
- In elementary reaction molecularity is equal to its order.
- In complex reaction molecularity of each step of mechanism is defined separately.
- Total molecularity of complex reaction is meaningless.
- In complex reactions generally molecularity of slowest step is same as order of reaction which can be considered as molecularity of reaction. (Except when slowest step contain intermediate)
- Maximum value of molecularity or order is 3 because chances of effective collision of more than three molecules is very rare.

2.7 PSEUDO FIRST ORDER REACTION

A chemical reaction in which value of order of reaction is one but molecularity is more than one are known as pseudo unimolecular/pseudo first order reaction.

Example-1

Hydrolysis of ester in acidic medium.



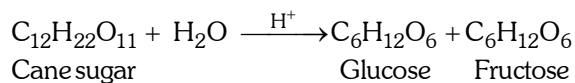
$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$$

Water is in excess then its concentration remain constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] \quad \text{where } k' = k [\text{H}_2\text{O}]$$

Example-2

Inversion of cane sugar.



$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}][\text{H}_2\text{O}]$$

Water is in excess then its concentration remain constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{C}_{12}\text{H}_{22}\text{O}_{11}] \quad \text{where } k' = k [\text{H}_2\text{O}]$$

GOLDEN KEY POINTS

- Reactant taken in excess can't affect order of reaction.
- In certain complex reaction product is also considered in order calculation.
- Order of reaction is determined experimentally.



Illustrations

Illustration 3. Give the following data for the reaction : $A + B \rightarrow \text{Product}$.

| Experiment No. | [A] | [B] | ROR ($\text{mol L}^{-1}\text{s}^{-1}$) |
|----------------|-----|-----|--|
| 1 | 1 | 2 | 4 |
| 2 | 2 | 2 | 4 |
| 3 | 2 | 4 | 16 |

What is the rate law equation ?

Solution. We know that rate law is given by : $r = k[A]^x[B]^y$ (1)

put the values of experiment No. 1 and 2 in equation 1, we get

$$4 = k[1]^x[2]^y \quad \text{.....(2)}$$

$$\text{and } 4 = k[2]^x[2]^y \quad \text{.....(3)}$$

Now, Equation (2) is divided by (3), we get

$$1 = \left(\frac{1}{2}\right)^x \quad \text{i.e., } x = 0$$

Now, put the values of experiment no. 2 and 3 in equation (1), we get

$$4 = (2)^x (2)^y \quad \text{.....(4)}$$

$$16 = (2)^x (4)^y \quad \text{.....(5)}$$

Equation (4) is divided by (5), we get

$$\frac{1}{4} = \left(\frac{1}{2}\right)^y \quad \text{i.e., } y = 2$$

So, order of reaction with respect to 'A' is 0 and with respect to 'B' is 2 and the rate of reaction is $r = k[A]^0[B]^2 = k[B]^2$ i.e., order of reaction = 2

Illustration 4. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by :

$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2}$$

The rate of reaction is followed by increase in pressure in a closed vessel and the rate can also be expressed in terms of the partial pressure of dimethyl ether i.e.,

$$\text{Rate} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?

Solution. $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2$

$$\text{Rate} = k[\text{CH}_3\text{OCH}_3]^{3/2} = k(P_{\text{CH}_3\text{OCH}_3})^{3/2}$$

Unit of rate = bar min^{-1}

$$\text{Unit of } k = \frac{\text{Rate}}{(P_{\text{CH}_3\text{OCH}_3})^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{ min}^{-1}$$



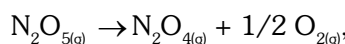
Illustration 5. For a reaction ; $3A \rightarrow \text{Products}$, it is found that the rate of reaction doubles if concentration of A is increased four times, calculate order of reaction.

Solution. Rate = $k[\text{Reactant}]^n$ if $[\text{Reactant}] = a$; rate = r_1
 $r_1 = k[a]^n$ if $[\text{Reactant}] = 4a$; rate = $2r_1$

$$2r_1 = k[4a]^n ; \frac{1}{2} = \left[\frac{1}{4}\right]^n \Rightarrow n = \frac{1}{2}$$

Illustration 6. For the decomposition, $N_2O_{5(g)} \rightarrow N_2O_{4(g)} + 1/2 O_{2(g)}$, the initial pressure of N_2O_5 is 114 mm and after 20 s the pressure of reaction mixture becomes 133 mm of Hg. Calculate the rate of reaction in terms of (a) change in atm s^{-1} and (b) change in molarity s^{-1} . Given that reaction is carried out at 127°C .

Solution.



Initial pressure P 0 0

Pressure at t = 20 s (P - P') P' P'/2

Given P = 114 mm

After 20 s, total pressure = (P - P') + P' + (P'/2) = 133 mm

$$\Rightarrow P'/2 = 19 \text{ mm} \quad P' = 38 \text{ mm}$$

Thus rate of reaction in terms of change in pressure = $38/20 = 1.9 \text{ mm s}^{-1}$

$$= \frac{1.9}{760} \text{ atm s}^{-1} = 2.5 \times 10^{-3} \text{ atm s}^{-1}$$

Also we have $PV = nRT$ or $\frac{n}{V} = C = \frac{P}{RT}$

\therefore change in concentration in 20 second = $\Delta C = \frac{P'}{RT}$ (change in pressure)

$$= \frac{38}{760 \times 0.0821 \times 400} = 1.52 \times 10^{-3} \text{ M}$$

\therefore rate of reaction in terms of change in concentration = $\frac{1.52 \times 10^{-3}}{20} = 7.61 \times 10^{-5} \text{ M s}^{-1}$

BEGINNER'S BOX-2

1. $A_2 + B_2 \rightarrow 2AB$; R.O.R. = $k[A_2]^a[B_2]^b$

| $[A_2]$ | $[B_2]$ | Rate of reaction $[\text{Ms}^{-1}]$ |
|---------|---------|-------------------------------------|
| 0.2 | 0.2 | 0.04 |
| 0.1 | 0.4 | 0.04 |
| 0.2 | 0.4 | 0.08 |

order of reaction with respect to A_2 and B_2 are respectively :

(1) a = 1, b = 1 (2) a = 2, b = 0 (3) a = 2, b = 1 (4) None

2. For a reaction the initial rate is given as : $R_0 = k[A]_0^2[B]_0$ by what factor, the initial rate of reaction will increase if initial concentration of A is 1.5 times and B is tripled ?

(1) 4.5 (2) 2.25 (3) 6.75 (4) None of these

3. For $A_{(g)} + B_{(g)} \rightarrow C_{(g)}$; rate = $k[A]^{1/2}[B]^2$, if initial concentration of A and B are increased by factor of 4 and 2 respectively, then the initial rate is changed by the factor :-

(1) 4 (2) 6 (3) 8 (4) None of these

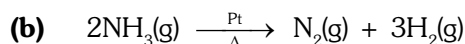
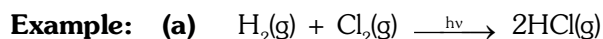


2.8 STUDY OF DIFFERENT ORDER REACTIONS :

(A) Zero order reactions

Reactions in which rate of reaction remains independent of concentration of the reactant are said to be zero order reactions.

- Zero order reactions are relatively uncommon but they occur under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.

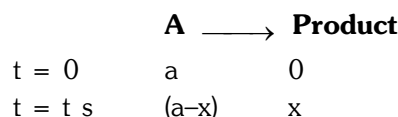


(c) Reaction between Acetone and Bromine.

(d) Dissociation of HI on gold surface.

(e) Adsorption of gases on metal surface :- At low P, rate of adsorption is proportional to surface area covered which is proportional to P or concentration of gas hence order is 1 whereas at high P, complete surface gets covered by gas & rate becomes independent of P & concentration hence order is 0.

Differential Rate Equation

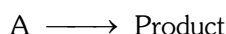


$$-\frac{d[A]}{dt} = k[A]^0$$

$$\frac{dx}{dt} = k[A]^0$$

Calculation of Rate Constant

Let us take the reaction



$$-\frac{d[A]}{dt} = k[A]^0 = k$$

$$-\int d[A] = \int k dt$$

$$-[A]_t = kt + C$$

$$\text{at } t = 0 \quad [A]_t = [A]_0$$

$$-[A]_0 = k \times 0 + C$$

$$C = -[A]_0$$

On substituting the value of C

$$-[A]_t = kt - [A]_0$$

$[A]_t = [A]_0 - kt$

 [Integrated rate equation]

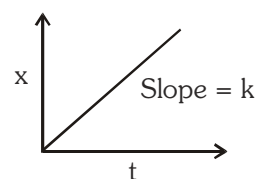
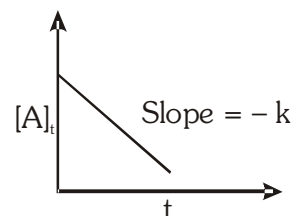
$$y = c - mx$$

$$[A]_0 - [A]_t = kt$$

$$k = \frac{[A]_0 - [A]_t}{t} = \frac{x}{t}$$

$x = kt$

x = Amount of reactant that will change in product.



- For zero order reaction, rate of reaction is equal to rate constant

Unit of rate constant

$k = \text{mol L}^{-1} \text{s}^{-1} = \text{unit of rate of reaction.}$

Half-life period – The time in which half of the initial amount of reactant is consumed.

$$\text{At } t = t_{1/2}, \quad [A]_t = \frac{[A]_0}{2}$$

$$\therefore k t_{1/2} = [A]_0 - \frac{[A]_0}{2} \quad \text{or} \quad t_{1/2} = \frac{[A]_0}{2k}$$

The half life period for a zero order reaction is directly proportional to the initial concentration of the reactants.

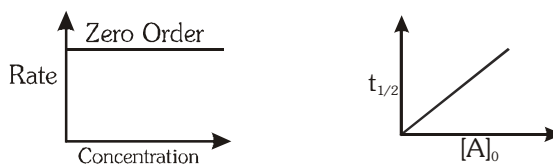
Time for completion of reaction

$$[A]_t = [A]_0 - kt$$

For completion $[A]_t = 0$

$$k = \frac{[A]_0}{t} \quad \boxed{t_{100\%} = \frac{[A]_0}{k}}$$

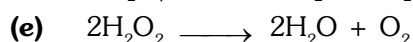
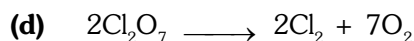
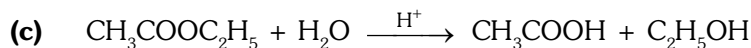
Graphical representation



(B) First order reactions

Reactions in which the rate of reaction is directly proportional to concentration of reactant.

Example :



Differential rate equation

| | A | Product |
|-------------------|-------|---------|
| $t = 0$ | a | 0 |
| $t = t \text{ s}$ | (a-x) | x |



$$-\frac{d[A]}{dt} = k[A] \quad \boxed{\frac{dx}{dt} = k(a-x)}$$

Calculation of rate constant

$$-\int \frac{d[A]}{[A]} = k \int dt$$

$$-\ln[A]_t = kt + c \quad \dots\dots\dots(i)$$

$$\text{At } t = 0; [A]_t = [A]_0 \therefore C = -\ln[A]_0$$

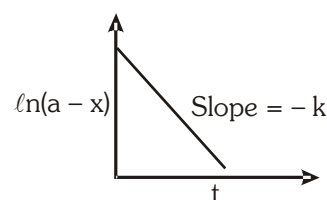
Putting the value of C in equation (i)

$$-\ln[A]_t = kt - \ln[A]_0$$

$$\boxed{\ln[A]_t = \ln[A]_0 - kt}$$

$$y = c - mx$$

$$\ln \frac{[A]_0}{[A]_t} = kt \quad \dots\dots\dots(ii) \quad \boxed{kt = \ln \left(\frac{a}{a-x} \right)}$$



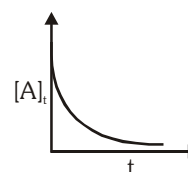
$$2.303 \log_{10} \frac{[A]_0}{[A]_t} = kt$$

$$\boxed{K = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}}$$

from equation(ii)

$$\frac{[A]_0}{[A]_t} = e^{kt}$$

$$\frac{[A]_t}{[A]_0} = e^{-kt} \Rightarrow \boxed{[A]_t = [A]_0 e^{-kt}} \text{ Wilhelmy equation}$$



Unit of rate constant [k = time⁻¹]

Half-life Period : The time in which half of the initial amount of reactant is consumed.

$$\text{At } t = t_{1/2} ; \quad x = a/2 ; \quad a-x = a/2$$

$$t_{1/2} = \frac{1}{k} \ln \left(\frac{a}{a/2} \right) \quad \text{or} \quad t_{1/2} = \frac{\ln 2}{k} = \frac{2.303}{k} (\log 2) \quad \text{or} \quad \boxed{t_{1/2} = \frac{0.693}{k}}$$

Half-life period for first order reaction is independent of the initial concentration of reactant.

Time for 3/4th of the Reaction (t_{3/4}) : The time in which 3/4th of the initial amount of reactant is consumed.

$$\text{At } t = t_{3/4} ; \quad x = 3a/4 ; \quad a-x = a/4$$



$$t_{3/4} = \frac{2.303}{k}(\log 4) = \frac{2.303}{k} \times 2 \log 2 = 2 \times t_{1/2}$$

$t_{3/4}$ for first order reaction is independent of the initial concentration of reactant.

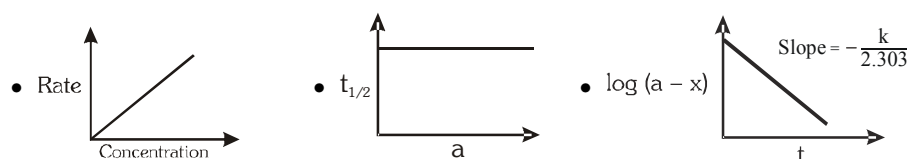
Interval Formula

$$k = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

where x_1 and x_2 are the amount consumed at time t_1 and t_2 respectively.

Time required for the completion of definite fraction of the first order reaction is independent of the initial concentration of the reactant.

Graphical Representation



(C) GENERAL INTEGRATED RATE EQUATION (n^{th} order kinetics)

$$kt = \frac{1}{(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right] \quad [n \neq 1]$$

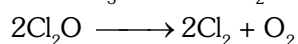
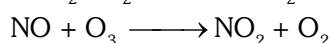
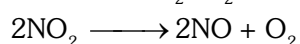
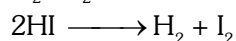
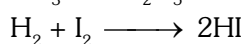
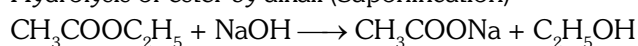
If $t = t_{1/2}$; $x = \frac{a}{2}$

Therefore $kt_{1/2} = \frac{1}{(n-1)} \left[\left(\frac{2}{a} \right)^{n-1} - \left(\frac{1}{a} \right)^{n-1} \right]$

$$kt_{1/2} = \frac{1}{(n-1)} \left[\frac{2^{n-1} - 1}{a^{n-1}} \right] \quad (n \neq 1) ; \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

(i) Second order reactions

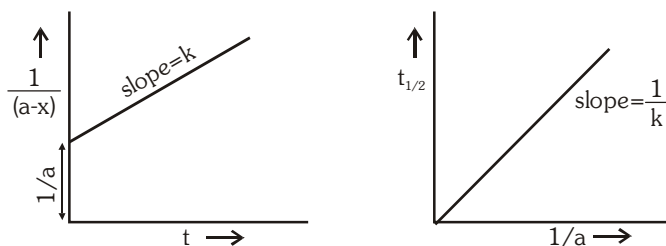
Hydrolysis of ester by alkali (Saponification)



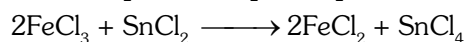
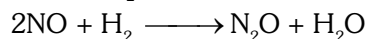
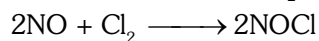
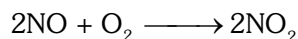
For second order : $n = 2$

$$kt = \frac{1}{(2-1)} \left[\frac{1}{(a-x)} - \frac{1}{a} \right] = \frac{1}{(a-x)} - \frac{1}{a}$$

Half life $t_{1/2} = \frac{1}{ak}$

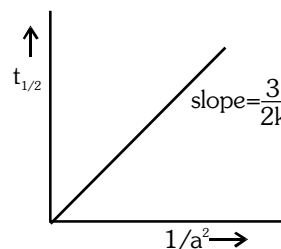
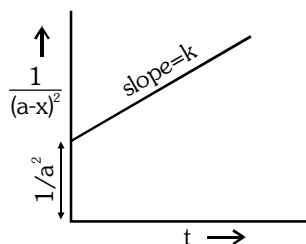


(ii) Third order reactions



for third order $n = 3$
$$kt = \frac{1}{(3-1)} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right] = \frac{1}{2} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

Half life
$$t_{1/2} = \frac{3}{2a^2k}$$



Examples of fractional order reaction

| Reaction | Order |
|---|-------|
| $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ | 1.5 |
| $\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$ | 2.5 |
| $\text{COCl}_2 \longrightarrow \text{CO} + \text{Cl}_2$ | 1.5 |
| $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$ | 1.5 |
| $\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$ | 1.5 |

Illustrations

Illustration 7. 90% of a first order reaction was completed in 10 hours. When will 99.9% of the reaction complete ?

Solution.
$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}, \quad a = 100, \quad x = 90, \quad t = 10$$

So
$$k_1 = \frac{2.303}{10} \log \frac{100}{10} = 2.303 \times 10^{-1} \text{ hour}^{-1}$$

Now for 99.9% completion : $a = 100$ and $x = 99.9$

$$t = \frac{2.303}{k_1} \log \frac{100}{0.1} = \frac{2.303}{2.303 \times 10^{-1}} \times 3 = 30 \text{ hours}$$

Illustration 8. 20% of a first order reaction was completed in 5 min. When will 60% of the reaction complete ?

Solution. $t = 5 \text{ min}$, $a = 100$, $x_1 = 20$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x_1} \right) = \frac{2.303}{5} \log \frac{100}{80} = \frac{2.303}{5} \log \frac{5}{4} = \frac{2.303}{5} [\log 5 - \log 4]$$

$$k = \frac{2.303}{5} [0.6989 - 0.6020] = \frac{2.303}{5} [0.0969] = 0.0446$$

Now $x_2 = 60$

$$k = \frac{2.303}{t} \log \left(\frac{a}{a-x_2} \right)$$

$$t = \frac{2.303}{0.0446} \log \frac{100}{40} = \frac{2.303}{0.0446} [\log 5 - \log 2] = \frac{2.303}{0.0446} \times 0.3979 = 20.55 \text{ min.}$$



Illustration 9. For the first order reaction, half life is 6 min. Calculate the rate constant of the reaction ?

Solution. $t_{1/2} = \frac{0.693}{k_1} \Rightarrow k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{6} = 0.1155 \text{ min}^{-1}$

Illustration 10. A first order reaction is 90% complete in 40 min. Calculate the Half life of the reaction.

Solution. $a = 100, x = 90$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{100}{10} = \frac{2.303}{40} = 5.757 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k_1} = \frac{0.693}{5.757 \times 10^{-2}} = 12.03 \text{ min.}$$

Illustration 11. In a second order reaction both the reactants have equal initial concentration, the time taken for 60% completion of reaction is 3000 s. What will be the time taken for 20% of the reaction?

Solution. $k_2 = \frac{1}{t} \frac{x}{a(a-x)}, \quad \text{Let } a = 1,$

$$k_2 = \frac{1}{t} \frac{x}{a(1-x)} = \frac{1}{3000} \left(\frac{0.6}{1-0.6} \right) = \frac{1}{3000} \times \frac{0.6}{0.4} = \frac{1}{2000}$$

So time for the 20% completion is :

$$t = \frac{1}{k_2} \frac{x}{a(a-x)} = 2000 \times \frac{0.20}{0.80} = 500 \text{ s.}$$

Illustration 12. If the initial concentration of reactants are doubled then half life becomes half. Calculate order of the reaction ?

Solution. $\frac{\left(\frac{t_1}{2}\right)_1}{\left(\frac{t_1}{2}\right)_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \Rightarrow \frac{\left(\frac{t_1}{2}\right)_1}{\left(\frac{t_1}{2}\right)_2} = \left(\frac{2a}{a}\right)^{n-1}$

$$2 = (2)^{n-1} \Rightarrow n - 1 = 1 \Rightarrow n = 2$$

so, the order of the reaction will be 2.

BEGINNER'S BOX-3

1. Which of the following expressions is correct for zero order and first order reactions respectively (where a is initial concentration) ?

(1) $t_{1/2} \propto a; t_{1/2} \propto \frac{1}{a}$ (2) $t_{1/2} \propto a; t_{1/2} \propto a^0$ (3) $t_{1/2} \propto a^0; t_{1/2} \propto a$ (4) $t_{1/2} \propto a; t_{1/2} \propto \frac{1}{a^2}$

2. For the zero order reaction, $A \rightarrow B + C$; initial concentration of A is 0.1 M. If $[A] = 0.08 \text{ M}$ after 10 minutes, then it's half-life and completion time are respectively :

(1) 10 min; 20 min (2) $2 \times 10^{-3} \text{ min}; 4 \times 10^{-3} \text{ min}$
(3) 25 min, 50 min (4) 250 min, 500 min

3. For an elementary reaction, $X(g) \rightarrow Y(g) + Z(g)$ the half life period is 10 min. In what period of time the concentration of X will be reduced to 10% of original concentration?

(1) 20 min (2) 33 min (3) 15 min (4) 25 min

4. A first order reaction is 75% completed in 100 min. How long will it take for it's 87.5% completion?

(1) 125 min (2) 150 min (3) 175 min (4) 200 min

5. The rate constant for a first order reaction which has half life 480 s is :-

(1) $1.44 \times 10^{-3} \text{ s}^{-1}$ (2) $1.44 \times \text{s}^{-1}$ (3) $0.72 \times 10^{-3} \text{ s}^{-1}$ (4) $2.88 \times 10^{-3} \text{ s}^{-1}$



2.9 COLLISION THEORY OF CHEMICAL REACTIONS

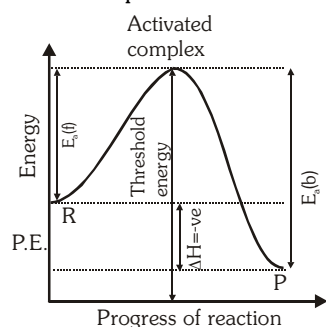
This theory was given by Max Trautz and William Lewis. According to it, for a reaction to occur there must be collisions in between reacting molecules. Total number of collisions per second in unit volume is called collision frequency (z). Generally its value is very high for gaseous reactions (10^{25} to 10^{28} collisions/sec-cm³). But only a small fraction of these collisions are capable to convert reactant into product. These collisions are called as effective collisions.

For effective collision following two conditions must be satisfied at a time :

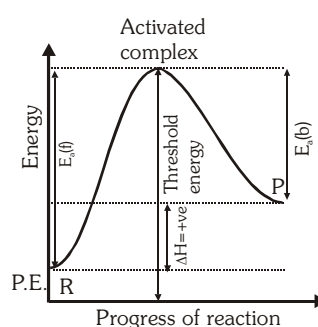
(a) Reacting molecules must possess a minimum amount of energy.

(b) Proper orientation of collision

- **Threshold energy** : The minimum energy which must be possessed by reacting molecules for a chemical reaction to occur.
- **Activation energy** : The minimum extra amount of energy required by reactant molecules for converting into products.



Exothermic reaction



Endothermic reaction

1. $E_a(f)$ = Activation energy for forward reaction
2. $E_a(b)$ = Activation energy for backward reaction

If not specified in questions then consider E_a for forward reaction.

$$\Delta H = E_{a(f)} - E_{a(b)} \quad ; \quad \Delta H = H_p - H_R$$

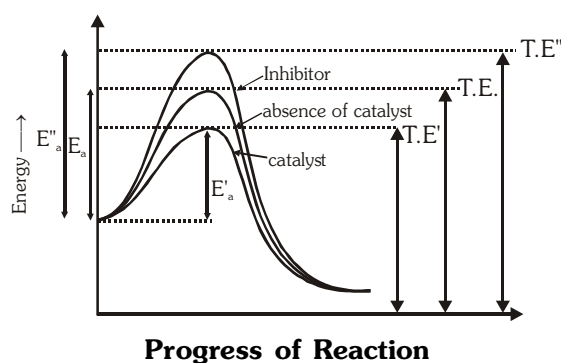
ACTIVATION ENERGY MAINLY DEPENDS UPON :

(i) **Nature of reactant** : For different reactants, number of bonds and bond energies are different, therefore activation energy will also be different.

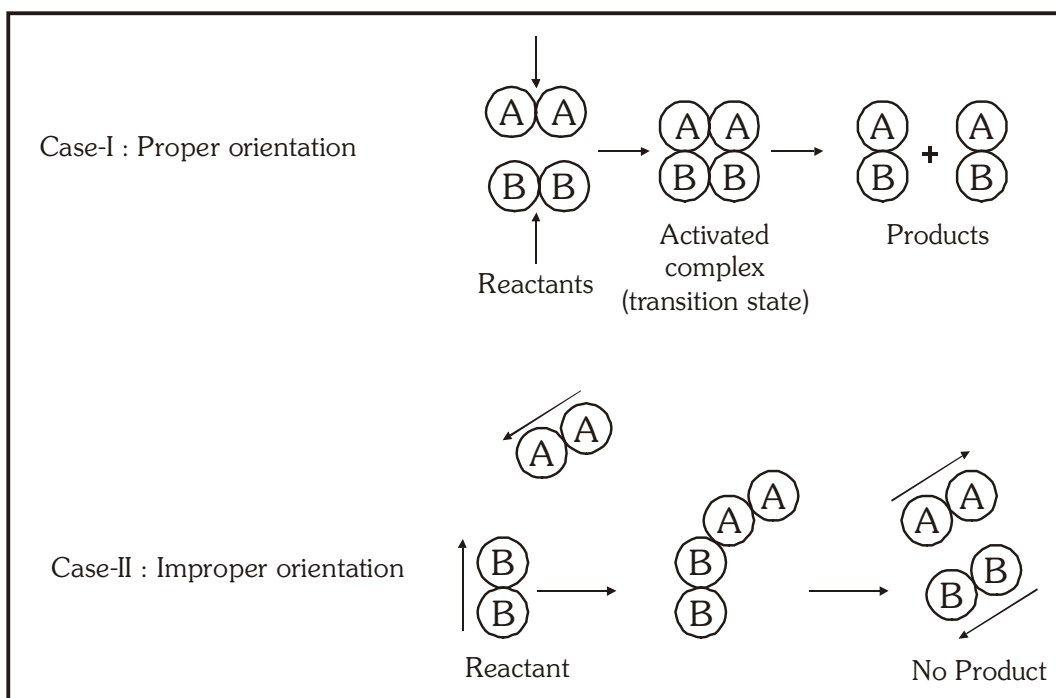
Reactions which have less E_a , take place at faster rate.

(ii) **Presence of catalyst** : Catalyst provide an alternative path of reaction mechanism for the reaction.

- In presence of catalyst threshold energy decreases, activation energy decreases and rate of reaction increases.
- In presence of negative catalyst (inhibitor) threshold energy increases, activation energy increases, rate of reaction decreases.



(b) Orientation :



• **Limitations :**

- (i) This theory is mainly applicable for gaseous reactions and also for solutions in which reacting species are molecules.
- (ii) This theory is mainly applicable for simple bimolecular reactions but fails for complex reactions.
- (iii) It considers molecules to be hard sphere and ignore structural aspect of molecules.

GOLDEN KEY POINTS

- Activated complex is most unstable complex formed in the transition state with effective collision.
- On increasing temperature E_a for reaction does not decrease but number of active molecules which are crossing the energy barrier increases therefore rate of reaction increases.
- According to Arrhenius ; rate of reaction $\propto e^{-\frac{E_a}{RT}}$ E_a = Activation energy
 R = Gas constant
 T = Temperature (in K)

Illustrations

Illustration 13 The E_a for an exothermic reaction $A \rightarrow B$ is 80 kJ mol^{-1} . Heat of reaction is 20 kJ mol^{-1} . E_a for the reaction $B \rightarrow A$ will be ?

Solution $\Delta H = E_{a(f)} - E_{a(b)} \Rightarrow -20 = 80 - E_{a(b)}$
 $E_{a(b)} = 100 \text{ kJ mol}^{-1}$

Illustration 14 For the reaction $A + B \rightleftharpoons C + D$ the activation energy is 32 kJ mol^{-1} . For the reverse reaction the E_a is 58 kJ mol^{-1} . Determine (i) Nature of reaction (ii) ΔH

Solution $\Delta H = E_{a(f)} - E_{a(b)}$
 $\Delta H = 32 - 58$
 $\Delta H = -26 \text{ kJ mol}^{-1}$ (exothermic)

Illustration 15 For an endothermic reaction

- (1) $E_a > \Delta H$
- (2) $E_a < \Delta H$
- (3) $E_a = \Delta H$
- (4) any one of the above

Solution **Ans. (1)**



Illustration 16 For an exothermic reaction

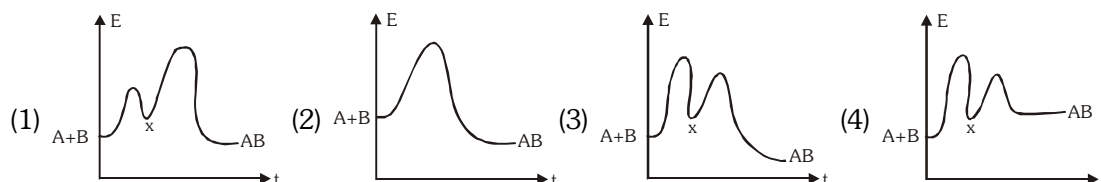
- (1) $E_a > \Delta H$ (2) $E_a < \Delta H$ (3) $E_a = \Delta H$ (4) any one of the above

Solution **Ans. (4)**

Illustration 17 An exothermic chemical reaction is occurring in two steps as follows

- (i) $A + B \rightarrow X$ (slow) (ii) $X \rightarrow AB$ (fast)

the process of reaction can be best described by



Solution **Ans. (3)**

2.10 FACTORS AFFECTING RATE OF REACTION :

1. Nature of reactant :

(a) Physical state of reactant :

increasing order of rate of reaction – Solid < liquid < gas

(Intermolecular attractive force decreases which provides more freedom for collisions)

(b) Physical size of particles (if reactant is solid) :

$$\text{Rate of reaction} \propto \frac{1}{\text{physical size}} \propto \text{surface area}$$

(c) **Chemical nature of reactant** : For different reacting species number of bonds broken and their bond energies are different. Therefore requirement of activation energy is also different. Now reactions having less value of activation energy will take place at faster rate.

2. Concentration of reactant : Rate of reaction \propto concentration of reactant

3. **Pressure** : Effect of pressure on Rate of reaction is negligible when reactants are solid or liquid. But if reactants are in gaseous state then rate of reaction increases on increasing pressure because number of effective collisions increases.

4. **Temperature** : On increasing temperature rate of reaction increases whether the reaction is exothermic or endothermic. When temperature increases KE of molecules increases, number of activated molecules increases thus rate of reaction increases.

Relation between rate constant and Temperature :-

(a) Generally it is found that for every 10 °C rise in temperature Rate of reaction becomes 2 to 3 times.

Temperature coefficient (μ) : It is defined as ratio of rate constant of a reaction at two different temperatures which will be differ by 10 °C.

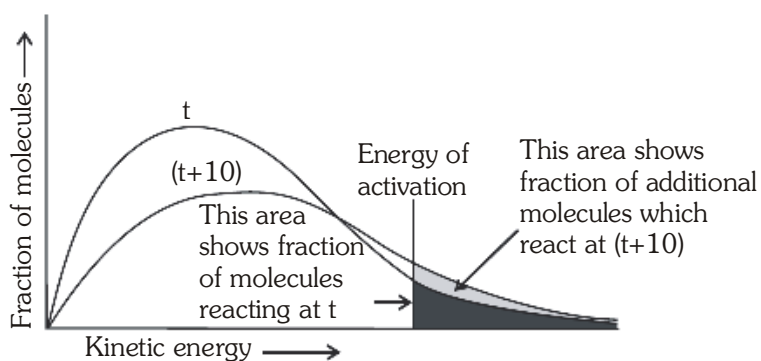
$$\mu = \frac{k_{T+10}}{k_T} = 2 \text{ to } 3 ; \quad \frac{r_2}{r_1} = \frac{k_2}{k_1} = \mu^{\Delta T/10}$$

If temperature of reaction is not specified then consider 25 °C.

(If μ is not given consider it as minimum 2)



MAXWELL AND BOLTZMANN ENERGY DISTRIBUTION CURVE



(b) Arrhenius equation

$$k = Ae^{-E_a/RT} \quad \dots(1)$$

A = Arrhenius constant / pre-exponential factor / Frequency factor

E_a = Activation energy

R = gas constant

T = Temperature (Kelvin)

- k increases with increase in temperature

If $T \rightarrow \infty$; $k = A$

- $\frac{k}{A} = e^{-E_a/RT}$ = fraction of molecules having energy $\geq E_a$

$e^{-E_a/RT}$ = Boltzman factor

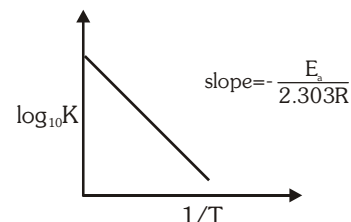
On taking logarithm for equation (1) on both sides.

$$\ln k = \ln A + \ln e^{-E_a/RT}$$

$$2.303 \log_{10} k = 2.303 \log_{10} A - \frac{E_a}{RT}$$

$$\boxed{\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}} \quad \dots(2)$$

$y = c - mx$



- E_a of reaction can be determined by measuring rate constant at two different temperatures
At temperature T_1 :

$$\log_{10} k_1 = \log_{10} A - \frac{E_a}{2.303RT_1} \quad \dots(3)$$

At temperature T_2 :

$$\log_{10} k_2 = \log_{10} A - \frac{E_a}{2.303RT_2} \quad \dots(4)$$

Equation (4) – Equation (3) gives -

$$\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\boxed{\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)}$$



- From Arrhenius equation - $k = Ae^{-E_a/RT}$

$$\ln k = \ln A - \frac{E_a}{RT}$$

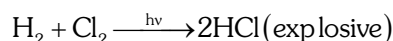
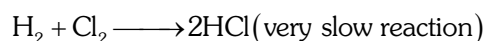
$$\frac{d}{dT}(\ln k) = \frac{d}{dT}(\ln A) + \frac{d}{dT}\left(-\frac{E_a}{RT}\right) = 0 - \frac{E_a}{R} \frac{d}{dT}(T^{-1}) = \frac{E_a}{R}(T^{-2})$$

$$\boxed{\frac{d}{dT} \ln k = \frac{E_a}{RT^2}} \text{ differential form of Arrhenius equation}$$

5. Presence of catalyst : In presence of catalyst E_a of reaction decreases and rate of reaction increases.

6. Exposure to radiation : Rate of some reactions also increases when reaction are carried out in the presence of radiation. (only for photochemical reaction)

e.g. formation of HCl



GOLDEN KEY POINTS

● PHOTO CHEMICAL REACTION

Reactions which occur in presence of light are photochemical reaction i.e., reaction which do not occur in dark.

Example : (i) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$ **(ii)** Photo synthesis **(iii)** Vision

- In photochemical reaction, each molecule of the reacting substance absorbs one quantum (single photon) of radiation and is activated to form the product.
- For every reaction, a certain amount of energy is required.
- Higher the intensity of light greater will be the rate of reaction.
- For these reactions, the value of ΔG may be positive or negative.
- Temperature have no significant effect.

Mechanism : $Cl_2 + h\nu \longrightarrow Cl_2^*$ (activated molecule)

Primary step of reaction : $Cl_2^* \longrightarrow Cl + Cl$

Secondary step of reaction : $H_2 + Cl \longrightarrow HCl + H$

$Cl_2 + H \longrightarrow HCl + Cl$

Final step of reaction : $Cl + Cl \longrightarrow Cl_2$

● Quantum yield (or quantum efficiency) :

The quantum efficiency yield (ϕ) of a photochemical reaction may be expressed as

$$\phi = \frac{\text{Number of molecules reacted or product formed}}{\text{Number of photons absorbed}}$$

● Application of Photochemical Reaction

- | | | |
|---------------------------|-------------------------------------|---|
| (i) In photography | (ii) In photo printing | (iii) In photosynthesis |
| (iv) In vision | (v) In electronic industries | (vi) In many polymerization reactions. |



Illustrations

Illustration 18 A reaction whose temperature is increased from 10 °C to 50 °C then increase in rate of reaction will be—

Solution. We know that on increasing temperature by 10°C the rate of reaction becomes 2 to 3 times.

Note : If the value of temperature coefficient is not given then we will take 2.

$$\begin{aligned} 10\text{ }^{\circ}\text{C} &\text{—} & 20\text{ }^{\circ}\text{C} &= 2 \text{ times} \\ 20\text{ }^{\circ}\text{C} &\text{—} & 30\text{ }^{\circ}\text{C} &= 2^2 \text{ times} \\ 30\text{ }^{\circ}\text{C} &\text{—} & 40\text{ }^{\circ}\text{C} &= 2^3 \text{ times} \\ 40\text{ }^{\circ}\text{C} &\text{—} & 50\text{ }^{\circ}\text{C} &= 2^4 \text{ times} \\ && &= 16 \text{ times} \end{aligned}$$

Illustration 19 For a reaction, temperature coefficient = 2, then calculate the activation energy (in kJ) of the reaction.

Solution. Let $T_1 = 25\text{ }^{\circ}\text{C}$, $T_2 = 35\text{ }^{\circ}\text{C}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Given : Temperature coefficient = $\frac{k_2}{k_1} = 2$

$$T_1 = 25 + 273 = 298\text{ K}, T_2 = 35 + 273 = 308\text{ K}, R = 8.314$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{10}{298 \times 308} \right)$$

$$E_a = 52.897\text{ kJ}$$

Illustration 20 An exothermic reaction $A \longrightarrow B$ has an activation energy of 17 kJ mol⁻¹ of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction $B \longrightarrow A$.

Solution. For the reaction $A \longrightarrow B$.

Activation energy $E_a = 17\text{ kJ}$

$$\Delta H = -40\text{ kJ}$$

$$\Delta H = E_a(f) - E_a(b)$$

$$E_a(b) = 17 - (-40) = 57\text{ kJ}$$

Illustration 21 For first order gaseous reaction $\log k$ when plotted against $\frac{1}{T}$, gives a straight line with a slope of -8000. Calculate the activation energy of the reaction.

Solution. Arrhenius equation $k = Ae^{-E_a/RT}$

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T}$$

when curve is plotted between $\log k$ and $\frac{1}{T}$, a straight line is obtained. Slope of this line = $-\frac{E_a}{2.303R}$

$$\text{Then, } \frac{E_a}{2.303R} = 8000 \text{ or } E_a = 8000 \times 2.303 \times 1.987 = 36608\text{ Cal}$$

Illustration 22 If temperature of a reaction is increased from 10°C to 100°C then how many times rate of reaction will become?

Solution 2^9 times

Illustration 23 If temperature of a reaction is increased from t_1 to t_2 then rate of reaction becomes ?

Solution $(\mu)^{t_2-t_1/10} \Rightarrow (\mu)^{\Delta T/10}$ times ; $r_{\text{new}} = r_{\text{old}} \times (\mu)^{\Delta T/10}$

Illustration 24 A reaction is carried out at 10°C. If temperature is increased by 50°C then how many times rate of reaction will become?

Solution 32 times



BEGINNER'S BOX-4

1. For an endothermic reaction where ΔH represents the enthalpy of reaction in kJ mol^{-1} , the minimum value for the energy of activation will be

(1) less than ΔH
(2) more than ΔH

(3) equal to ΔH
(4) zero

2. The activation energy of the reaction, $A + B \rightarrow C + D + 38 \text{ kcal}$ is 20 kCal, what would be the activation energy of the reaction, $C + D \rightarrow A + B$

(1) 20 kCal
(2) - 20 kCal

(3) 18 kCal
(4) 58 kCal

3. $\frac{k_{35^\circ}}{k_{34^\circ}} > 1$, this means that

(1) Rate increases with the rise in temperature
(2) Rate decreases with rise in temperature

(3) rate does not change with rise in temperature
(4) None of the above

4. The plot of $\ln k$ versus $1/T$ is linear with slope of

(1) $-\frac{E_a}{R}$
(2) $\frac{E_a}{R}$

(3) $\frac{E_a}{2.303R}$
(4) $-\frac{E_a}{2.303R}$

ANSWER KEY

| | | | | | | | | | | | |
|-------------------------|------|---|---|---|--|--|--|--|--|--|--|
| BEGINNER'S BOX-1 | Que. | 1 | 2 | 3 | | | | | | | |
| | Ans. | 1 | 3 | 3 | | | | | | | |

| | | | | | | | | | | | |
|-------------------------|------|---|---|---|--|--|--|--|--|--|--|
| BEGINNER'S BOX-2 | Que. | 1 | 2 | 3 | | | | | | | |
| | Ans. | 1 | 3 | 3 | | | | | | | |

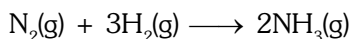
| | | | | | | | | | | | |
|-------------------------|------|---|---|---|---|---|--|--|--|--|--|
| BEGINNER'S BOX-3 | Que. | 1 | 2 | 3 | 4 | 5 | | | | | |
| | Ans. | 2 | 3 | 2 | 2 | 1 | | | | | |

| | | | | | | | | | | | |
|-------------------------|------|---|---|---|---|--|--|--|--|--|--|
| BEGINNER'S BOX-4 | Que. | 1 | 2 | 3 | 4 | | | | | | |
| | Ans. | 2 | 4 | 1 | 1 | | | | | | |



EXERCISE-I (Conceptual Questions)**RATE OF REACTION**

1. Consider the chemical reaction :



The rate of this reaction can be expressed in terms of concentration of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst the rate expressions.

$$(1) \text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$(2) \text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{3d[\text{H}_2]}{dt} = \frac{2d[\text{NH}_3]}{dt}$$

$$(3) \text{Rate} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$(4) \text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$$

2. In the formation of sulphur trioxide by the contact process $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$; the rate of reaction is expressed as

$$-\frac{d[\text{O}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

The rate of disappearance of (SO_2) will be

- (1) $5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (2) $-2.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (3) $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (4) $50.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

3. In a catalytic reaction involving the formation of ammonia by Haber's process $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ the rate of appearance of NH_3 was measured as $2.5 \times 10^{-4} \text{ mole L}^{-1} \text{ s}^{-1}$. The rate of disappearance of H_2 will be -

- (1) $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (2) $1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (3) $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 (4) $5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

4. Which of the following statement is correct for a reaction $\text{X} + 2\text{Y} \rightarrow \text{Product}$

- (1) The rate of disappearance of X = twice the rate of disappearance of Y.
 (2) The rate of disappearance of X = $\frac{1}{2}$ rate of appearance of products
 (3) The rate of appearance of products = $\frac{1}{2}$ the rate of disappearance of Y
 (4) The rate of appearance of products = $\frac{1}{2}$ the rate of disappearance of X

5. For the reaction, $\text{N}_2\text{O}_5 \longrightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$

$$\text{Given } -\frac{d[\text{N}_2\text{O}_5]}{dt} = K_1[\text{N}_2\text{O}_5], \frac{d[\text{NO}_2]}{dt} = K_2[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{O}_2]}{dt} = K_3[\text{N}_2\text{O}_5]$$

The relation between K_1 , K_2 and K_3 is -

- (1) $2K_1 = K_2 = 4K_3$ (2) $K_1 = K_2 = K_3$
 (3) $2K_1 = 4K_2 = K_3$ (4) None

6. Rate of formation of SO_3 according to the reaction $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ is $1.6 \times 10^{-3} \text{ kg min}^{-1}$. Hence rate at which SO_2 reacts is :-

- (1) $1.6 \times 10^{-3} \text{ kg min}^{-1}$
 (2) $8.0 \times 10^{-4} \text{ kg min}^{-1}$
 (3) $3.2 \times 10^{-3} \text{ kg min}^{-1}$
 (4) $1.28 \times 10^{-3} \text{ kg min}^{-1}$

7. For a general chemical change $2\text{A} + 3\text{B} \rightarrow \text{products}$, the rate of disappearance of A is r_1 and of B is r_2 . The rates r_1 and r_2 are related as :-

- (1) $3r_1 = 2r_2$ (2) $r_1 = r_2$
 (3) $2r_1 = 3r_2$ (4) $r_1^2 = 2r_2^2$

8. In a reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ the rate of appearance of NH_3 is $2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. The Rate of reaction & rate of disappearance of H_2 will be ($\text{In mol L}^{-1} \text{ sec}^{-1}$)

- (1) 3.75×10^{-4} , 1.25×10^{-4}
 (2) 1.25×10^{-4} , 2.5×10^{-4}
 (3) 1.25×10^{-4} , 3.75×10^{-4}
 (4) 5.0×10^{-4} , 3.75×10^{-4}

9. Which of the following statement is not correct for the reaction: $4\text{A} + \text{B} \rightarrow 2\text{C} + 2\text{D}$

- (1) The rate of disappearance of B is twice the rate of appearance of C
 (2) The rate of disappearance of B is one fourth the rate of disappearance of A
 (3) The rate of formation of D is one half the rate of consumption of A
 (4) The rate of formation of C and D are equal

10. For gaseous reaction, rate = $k[\text{A}][\text{B}]$. If volume of container is reduced to $\frac{1}{4}$ of initial, then the rate of the reaction will be..... times of initial:-

- (1) $\frac{1}{8}$ (2) 8 (3) $\frac{1}{16}$ (4) 16



11. $2A_{(g)} + B_{(g)} \rightleftharpoons \text{Product}$ is an elementary reaction, If pressure is increased three times of the initial pressure, the velocity of forward reaction will be ----- of the previous velocity:-

- (1) 9 times (2) 27 times
(3) $\frac{1}{9}$ times (4) $\frac{1}{27}$ times

RATE LAW / ORDER / MOLECULARITY

12. The rate of certain hypothetical reaction
 $A + B + C \rightarrow \text{products}$ is given by

$$r = \frac{-d[A]}{dt} = K[A]^{\frac{1}{2}}[B]^{\frac{1}{3}}[C]^{\frac{1}{4}}$$

The order of the reaction –

- (1) 1 (2) $\frac{1}{2}$ (3) 2 (4) $\frac{13}{12}$

13. Which of the following rate law has an overall order of 0.5 for reaction involving substances x,y and z ?

- (1) Rate = $K(C_x)(C_y)(C_z)$
(2) Rate = $K(C_x)^{0.5}(C_y)^{0.5}(C_z)^{0.5}$
(3) Rate = $K(C_x)^{1.5}(C_y)^{-1}(C_z)^0$
(4) Rate = $K(C_x)(C_z)^0 / (C_y)^2$

14. A chemical reaction involves two reacting species. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The order of reaction is –

- (1) 1 (2) 2
(3) Zero (4) Unpredictable

15. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the experimental data suggests, Rate = $K[H_2][Br_2]^{\frac{1}{2}}$. The order for this reaction is –

- (1) 2 (2) $1\frac{1}{2}$ (3) 1 (4) $2\frac{1}{2}$

16. Select the rate law that corresponds to the data shown for the following reaction $A + B \rightarrow C$

| Exp. | [A] | [B] | Initial rate |
|------|-------|-------|--------------|
| 1. | 0.012 | 0.035 | 0.10 |
| 2. | 0.024 | 0.070 | 1.6 |
| 3. | 0.024 | 0.035 | 0.20 |
| 4. | 0.012 | 0.070 | 0.80 |

- (1) Rate = $K[B]^3$ (2) Rate = $K[B]^4$
(3) Rate = $K[A][B]^3$ (4) Rate = $K[A]^2[B]^2$

17. In a certain gaseous reaction between X and Y,
 $X + 3Y \rightarrow XY_3$ The initial rates are reported as follows –

| [X] | [Y] | Rate |
|-------|-------|-------------------------|
| 0.1 M | 0.1 M | 0.002 Ms^{-1} |
| 0.2 M | 0.1 M | 0.002 Ms^{-1} |
| 0.3 M | 0.2 M | 0.008 Ms^{-1} |
| 0.4 M | 0.3 M | 0.018 Ms^{-1} |

The rate law is –

- (1) $r = K[X][Y]^3$ (2) $r = K[X]^q[Y]^2$
(3) $r = K[X][Y]$ (4) $r = [X]^q[Y]^3$

18. Select the law that corresponds to data shown for the following reaction $2A + B \rightarrow C + D$:-

| Exp. | [A] | [B] | Initial rate ($\text{mol L}^{-1} \text{ min}^{-1}$) |
|------|-----|-----|--|
| 1. | 0.1 | 0.1 | 7.5×10^{-3} |
| 2. | 0.3 | 0.2 | 9.0×10^{-2} |
| 3. | 0.3 | 0.4 | 3.6×10^{-1} |
| 4. | 0.4 | 0.1 | 3.0×10^{-2} |

- (1) Rate = $K[A]^2[B]$ (2) Rate = $K[A][B]^2$
(3) Rate = $K[A][B]^3$ (4) Rate = $K[A][B]$

19. For a hypothetical reaction ; $A + B \rightarrow C$ the following data were obtained in three different experiments :-

| [A] (mol L^{-1}) | [B] (mol L^{-1}) | Rate of reaction ($\text{mol L}^{-1} \text{ min}^{-1}$) |
|--------------------------------|--------------------------------|--|
| 0.01 | 0.01 | 1.0×10^{-4} |
| 0.01 | 0.03 | 9.0×10^{-4} |
| 0.03 | 0.03 | 2.70×10^{-3} |

The rate law will be :-

- (1) $r = K[A]^2[B]$ (2) $r = K[A][B]^2$
(3) $r = K[A][B]$ (4) None of these

20. Calculate the order of the reaction w.r.t. A and B:

| [A] (mol L^{-1}) | [B] (mol L^{-1}) | Rate |
|--------------------------------|--------------------------------|----------------------|
| 0.05 | 0.05 | 1.2×10^{-3} |
| 0.10 | 0.05 | 2.4×10^{-3} |
| 0.05 | 0.10 | 1.2×10^{-3} |

- (1) 1 and 0 (2) 1 and 1
(3) 0 and 1 (4) None



21. For a chemical reaction $A + B \rightarrow \text{product}$, the order is one with respect to each A and B. Value of x and y from the given data is :-

| Rate ($\text{mol L}^{-1}\text{s}^{-1}$) | [A] | [B] |
|--|--------|--------|
| 0.10 | 0.20 M | 0.05 M |
| 0.40 | x | 0.05 M |
| 0.80 | 0.40 M | y |

- (1) 0.20, 0.80 (2) 0.80, 0.40
(3) 0.80, 0.20 (4) 0.40, 0.20
22. Time required to complete a half fraction of a reaction varies inversely to the concentration of reactant then the order of reaction is -
(1) Zero (2) 1
(3) 2 (4) 3
23. The rate law for the single step reaction $2A + B \rightarrow 2C$, is given by -
(1) Rate = $K[A][B]$ (2) Rate = $K[A]^2[B]$
(3) Rate = $K[2A][B]$ (4) Rate = $K[A]^2[B]^0$
24. For a reaction of the type $A + B \rightarrow \text{products}$, it is observed that doubling the concentration of A causes the reaction rate to be four times as great, but doubling the amount of B does not effect the rate. The rate equation is -
(1) Rate = $K [A][B]$
(2) Rate = $K [A]^2$
(3) Rate = $K[A]^2[B]$
(4) Rate = $K[A]^2[B]^2$
25. Point out incorrect statement.
(1) Rate law is an experimental value
(2) Law of mass action is a theoretical proposal
(3) Rate law is more informative than law of mass action for developing mechanism
(4) Rate law is always different from the expression of law of mass action.
26. For an elementary process $2X + Y \rightarrow Z + W$, the molecularity is -
(1) 2 (2) 1
(3) 3 (4) Unpredictable
27. For a reaction $A + B \rightarrow \text{products}$, the rate of the reaction was doubled when the concentration of A was doubled, the rate was again doubled when the concentration of A & B were doubled the order of the reaction with respect to A & B are:-
(1) 1, 1 (2) 2, 0
(3) 1, 0 (4) 0, 1

28. For the reaction $A + B \rightarrow \text{products}$, it is found that the order of A is 1 and the order of B is $\frac{1}{2}$.

When the concentration of both A and B are increased four times, the rate will increase by a factor of :-

- (1) 16 (2) 8 (3) 6 (4) 4

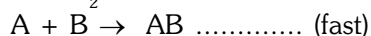
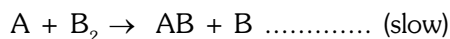
29. The rate law for a reaction $A + B \rightarrow \text{product}$ is rate = $K[A]^1[B]^2$. Then which one of the following statement is false :-
(1) If [B] is held constant while [A] is doubled, the reaction will proceed twice as fast
(2) If [A] is held constant while [B] is reduced to one quarter, the rate will be halved
(3) If [A] and [B] are both doubled, the reaction will proceed 8 times as fast
(4) This is a third order reaction
30. For a chemical reaction $A \rightarrow B$, the rate of reaction doubles when the concentration of A is increased 8 times. The order of reaction w.r.t. A is :-
(1) 3 (2) $\frac{1}{2}$ (3) $\frac{1}{3}$ (4) Zero
31. The specific rate constant of a first order reaction depends on the :-
(1) Concentration of the reactant
(2) Concentration of the product
(3) Time
(4) Temperature

PSEUDO FIRST ORDER REACTION / MECHANISM OF REACTION

32. Following mechanism has been proposed for a reaction $2A + B \rightarrow D + E$
 $A + B \rightarrow C + D$ (slow)
 $A + C \rightarrow E$ (fast)
 The rate law expression for the reaction is -
 (1) $r = K[A]^2[B]$ (2) $r = K[A][B]$
 (3) $r = K[A]^2$ (4) $r = K[A][C]$
33. The chemical reaction $2O_3 \rightarrow 3O_2$ proceeds as follows
 $O_3 \rightleftharpoons O_2 + O$ (fast)
 $O + O_3 \rightarrow 2O_2$ (slow)
 The rate law expression should be -
 (1) $r = K[O_3]^2$ (2) $r = K[O_3]^2[O_2]^{-1}$
 (3) $r = K[O_3][O_2]$ (4) Unpredictable



34. The hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism as given below –



The order of the over all reaction is –

- (1) 2 (2) 1 (3) $1\frac{1}{2}$ (4) Zero

35. The rate for the reaction

$RCl + NaOH(aq) \rightarrow ROH + NaCl$ is given by rate = $k_1[RCl]$. The rate of the reaction is –

- (1) Doubled on doubling the concentration of NaOH
(2) Halved on reducing the concentration of RCl to half
(3) Decreased on increasing the temperature of reaction
(4) Unaffected by increasing the temperature of the reaction

36. For reaction $NO_2 + CO \rightarrow CO_2 + NO$, the rate expression is, Rate = $k[NO_2]^2$

The number of molecules of CO involved in the slowest step will be –

- (1) 0 (2) 1
(3) 2 (4) 3

37. The rate law of the reaction $A + 2B \rightarrow \text{product}$

is given by $\frac{d[P]}{dt} = K[A]^2[B]$. If A is taken in large

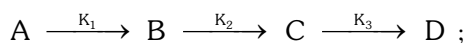
excess, the order of the reaction will be –

- (1) Zero (2) 1
(3) 2 (4) 3

38. The acid hydrolysis of ester is –

- (1) Psuedo 1st order reaction
(2) Bimolecular reaction
(3) Pseudo unimolecular reaction
(4) All

39. In the sequence of reaction



$K_3 > K_2 > K_1$, then the rate determining step of the reaction is :-

- (1) $A \rightarrow B$ (2) $C \rightarrow D$
(3) $B \rightarrow C$ (4) $A \rightarrow D$

40. The reaction mechanism for the reaction $P \rightarrow R$ is as follows :-

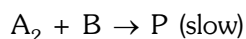
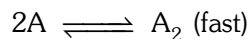


the rate law for the main reaction ($P \rightarrow R$) is

[where K_1 is an equilibrium constant]

- (1) $k_1[P][Q]$ (2) $k_1k_2[P]$
(3) $k_1k_2[P]^2$ (4) $k_1k_2[a]$

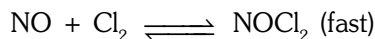
41. The reaction $2A + B \rightarrow P$, follows the mechanism



The order of the reaction is :-

- (1) 1.5 (2) 3 (3) 1 (4) 2

42. For the reaction $2NO + Cl_2 \rightarrow 2NOCl$ the following mechanism has been proposed



$NOCl_2 + NO \rightarrow 2NOCl$ (slow) the rate law for the reaction is :-

- (1) Rate = $K[NO]^2[Cl_2]$ (2) Rate = $K[NO][Cl_2]^2$
(3) Rate = $K[NOCl_2]$ (4) Rate = $K[NOCl]^2$

ZERO / FIRST / nth ORDER REACTIONS

43. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true at a moment for rate of all three reactions if concentration of reactants is same and greater than 1 M.

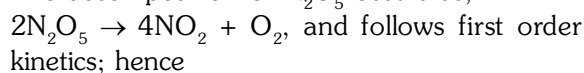
- (1) $r_1 = r_2 = r_3$ (2) $r_1 > r_2 > r_3$
(3) $r_1 < r_2 < r_3$ (4) All

44. K for a zero order reaction is

$2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$. If the concentration of the reactant after 25 s is 0.5 M, the initial concentration must have been.

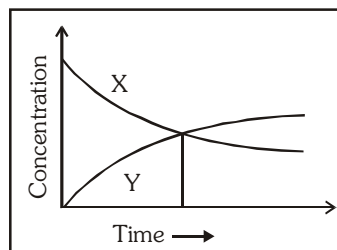
- (1) 0.5 M (2) 1.25 M
(3) 12.5 M (4) 1.0 M

45. The decomposition of N_2O_5 occurs as,



- (1) The reaction is bimolecular
(2) The reaction is unimolecular
(3) $t_{1/2} \propto a^0$
(4) $t_{1/2} \propto a^2$

46. The accompanying figure depicts the change in concentration of species X and Y for the reaction $X \rightarrow Y$ as a function of time the point of intersection of the two curves represents.



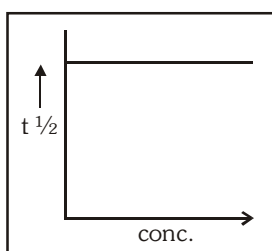
- (1) $t_{1/2}$
(2) $t_{3/4}$
(3) $t_{2/3}$
(4) Data are insufficient to predict



47. If the first order reaction involves gaseous reactants and gaseous products the unit of its rate is –
 (1) atm. (2) atm - s
 (3) atm - s⁻¹ (4) atm² s²
48. Plot of log(a - x) vs time t is straight line. This indicates that the reaction is of –
 (1) Second order (2) First order
 (3) Zero order (4) third order
49. The rate constant of a first order reaction is $4 \times 10^{-3} \text{ s}^{-1}$. At a reactant concentration of 0.02 M, the rate of reaction would be –
 (1) $8 \times 10^{-5} \text{ M s}^{-1}$ (2) $4 \times 10^{-3} \text{ M s}^{-1}$
 (3) $2 \times 10^{-1} \text{ M s}^{-1}$ (4) $4 \times 10^{-1} \text{ M s}^{-1}$
50. In a first order reaction the concentration of the reactant is decreased from 1.0 M to 0.25 M in 20 min. The rate constant of the reaction would be –
 (1) 10 min^{-1} (2) 6.931 min^{-1}
 (3) 0.6931 min^{-1} (4) 0.06931 min^{-1}
51. In a first order reaction the $a/(a - x)$ was found to be 8 after 10 minute. The rate constant is
 (1) $\frac{(2.303 \times 3 \log 2)}{10}$ (2) $\frac{(2.303 \times 2 \log 3)}{10}$
 (3) $10 \times 2.303 \times 2 \log 3$ (4) $10 \times 2.303 \times 3 \log 2$
52. 75 % of a first order reaction was found to complete in 32 min. When will 50 % of the same reaction complete –
 (1) 24 min (2) 16 min
 (3) 8 min (4) 4 min
53. A first order reaction has a half life period of 69.3 s. At 0.10 mol L⁻¹ reactant concentration, the rate will be –
 (1) 10^{-4} M s^{-1} (2) 10^{-3} M s^{-1}
 (3) 10^{-1} M s^{-1} (4) $6.93 \times 10^{-1} \text{ M s}^{-1}$
54. For a first order reaction $A \rightarrow$ products, the rate of reaction at $[A] = 0.2 \text{ M}$ is $1 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$. The half life period for the reaction is –
 (1) 832 min. (2) 440 s
 (3) 416 min. (4) 14 min.
55. 99 % of a first order reaction was completed in 32 min. when will 99.9 % of the reaction complete ?
 (1) 50 min. (2) 46 min.
 (3) 49 min. (4) 48 min.
56. The half life for the first order reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$ is 24 hrs. at 30°C. Starting with 10 g of N_2O_5 how many grams of N_2O_5 will remain after a period of 96 hours ?
 (1) 1.25 g (2) 0.63 g
 (3) 1.77 g (4) 0.5 g
57. What is the half life of a radioactive substance if 87.5% of any given amount of the substance disintegrate in 40 minutes ?
 (1) 160 min (2) 10 min
 (3) 20 min (4) 13 min 20 sec.
58. For a given reaction of first order it takes 20 minute for the concentration to drop from 1 M to 0.6 M. The time required for the concentration to drop from 0.6 M to 0.36 M will be :
 (1) More than 20 min
 (2) Less than 20 min
 (3) Equal to 20 min
 (4) Infinity
59. A first order reaction is carried out with an initial concentration of 10 mol per litre and 80% of the reactant changes into the product. Now if the same reaction is carried out with an initial concentration of 5 mol per litre for the same period the percentage of the reactant changing to the product is.
 (1) 40 (2) 80
 (3) 160 (4) Cannot be calculated
60. In the following first order reactions,
 $A + \text{Reagent} \rightarrow \text{Product}$, $B + \text{Reagent} \rightarrow \text{Product}$
 Calculate the ratio of K_1 / K_2 , 50% of B has been reacted, when 94% of A has been reacted –
 (1) 4.06 (2) 0.246
 (3) 2.06 (4) 0.06
61. The reaction $L \rightarrow M$ is started with 10 g/L. After 30 minute and 90 minute, 5 g/L and 1.25 g/L are left respectively. The order of reaction is
 (1) 0 (2) 2
 (3) 1 (4) 3
62. The doubling the initial concentration of a reactant doubles $t_{1/2}$ of the reaction, then order of the reaction is –
 (1) 3 (2) 2
 (3) 1 (4) 0
63. The half life period for catalytic decomposition of AB_3 at 50 mm is found to be 4 hrs and at 100 mm it is 2 hrs. The order of reaction is –
 (1) 3 (2) 1
 (3) 2 (4) 0



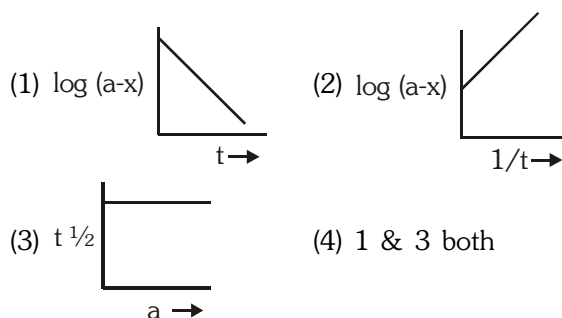
64. The rate constant for a reaction is $10.8 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$. The reaction obeys –
 (1) First order (2) Zero order
 (3) Second order (4) All are wrong
65. A substance 'A' decomposes in solution following the first order kinetics. Flask I contains 1 L of 1M solution of A and flask II contains 100 ml of 0.6 M solution. After 8 hr. the concentration of A in flask I becomes 0.25 M, what will be the time for concentration of A in flask II to become 0.3 M.
 (1) 0.4 hr.
 (2) 2.4 hr.
 (3) 4.0 hr.
 (4) Unpredictable as rate constant is not given
66. The rate constant (K) for the reaction $2A + B \rightarrow$ product, was found to be $2.5 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ after 15 s, $2.60 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ after 30 s and $2.55 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ after 50 s. The order of reaction is
 (1) 2 (2) 3 (3) Zero (4) 1
67. The rate constant for a second order reaction is $8 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$. How long will it take a 1M solution to be reduced to 0.5 M.
 (1) $8.665 \times 10^3 \text{ min}$ (2) $8 \times 10^{-3} \text{ min}$
 (3) $1.25 \times 10^4 \text{ min}$ (4) $4 \times 10^{-5} \text{ min}$
68. A graph between $t_{1/2}$ and concentration for n^{th} order reaction is a straight line. Reaction of this nature is completed 50% in 10 minutes when concentration is 2 mol L^{-1} . This is decomposed 50% in t minutes at 4 mol L^{-1} , n and t are respectively



- (1) 0, 20 min. (2) 1, 10 min.
 (3) 1, 20 min. (4) 0, 5 min.
69. In the first order reaction, 75% of the reactant disappeared in 1.388 h. Calculate the rate constant of the reaction :-
 (1) 1 s^{-1} (2) $2.8 \times 10^{-4} \text{ s}^{-1}$
 (3) $17.2 \times 10^{-3} \text{ s}^{-1}$ (4) $1.8 \times 10^{-3} \text{ s}^{-1}$

70. In the case of first order reaction, the ratio of time required for 99.9 % completion to 50 % completion is :-
 (1) 2 (2) 5 (3) 10 (4) None
71. From different sets of data of $t_{1/2}$ at different initial concentrations say 'a' for a given reaction, the $[t_{1/2} \times a]$ is found to be constant. The order of reaction is :-
 (1) 0 (2) 1 (3) 2 (4) 3
72. The reaction

$$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
 is first order with respect to N_2O_5 . Which of the following graph would yield a straight line :-
 (1) $\log(P_{\text{N}_2\text{O}_5})$ v/s time with negative slope
 (2) $P_{\text{N}_2\text{O}_5}^{-1}$ v/s time
 (3) $P_{\text{N}_2\text{O}_5}$ v/s time
 (4) $\log(P_{\text{N}_2\text{O}_5})$ v/s time with positive slope
73. Which of the following statement is not correct for the reaction whose rate is $r = k$ (rate constant)
 (1) rate of reaction is independent of concentration of reactant
 (2) $t_{1/2}$ of reaction is not depends upon concentration of reactant
 (3) rate constant is independent of concentration of reactant
 (4) this is zero order reaction
74. Which of the following curves represents a 1st order reaction :-



75. The following data were obtained at a certain temperature for the decomposition of ammonia
- | p (mm) | 50 | 100 | 200 |
|-----------|------|------|------|
| $t_{1/2}$ | 3.64 | 1.82 | 0.91 |
- The order of the reaction is :-
 (1) 0 (2) 1
 (3) 2 (4) 3



- 76.** A reaction is found to have the rate constant $\times s^{-1}$ by what factor the rate is increased if initial concentration of A is tripled
 (1) 3
 (2) 9
 (3) \times
 (4) Remains same
- 77.** Which is incorrect :-
 (1) Half life of a first order reaction is independent of initial concentration
 (2) Rate of reaction is constant for first order reaction
 (3) Unit of K for second order reaction is $\text{mol}^{-1} \text{L s}^{-1}$
 (4) Half life of zero order is proportional to initial concentration
- 78.** Hydrolysis of ester in alkaline medium is :-
 (1) First order reaction with molecularity one
 (2) Second order reaction with molecularity two
 (3) First order reaction with molecularity two
 (4) Second order reaction with molecularity one
- 79.** The expression which gives $\frac{1}{4}$ th life of 1st order reaction is :-
 (1) $\frac{K}{2.303} \log \frac{4}{3}$ (2) $\frac{2.303}{K} \log 3$
 (3) $\frac{2.303}{K} \log \frac{3}{4}$ (4) $\frac{2.303}{K} \log \frac{4}{3}$
- 80.** The rate constant of a zero order reaction is $0.2 \text{ mol dm}^{-3} \text{h}^{-1}$. If the concentration of the reactant after 30 minutes is 0.05 mol dm^{-3} . Then its initial concentration would be :-
 (1) 6.05 mol dm^{-3} (2) 0.15 mol dm^{-3}
 (3) 0.25 mol dm^{-3} (4) 4.00 mol dm^{-3}
- 81.** A reaction is of first order. After 100 minutes 75 gm of the reactant A are decomposed when 100 gm are taken initially, calculate the time required when 150 gm of the reactant A are decomposed, the initial weight taken is 200 gm :-
 (1) 100 minutes (2) 200 minutes
 (3) 150 minutes (4) 175 minutes
- 82.** For which of the following, the unit of rate and rate constant of the reaction are identical :-
 (1) First order reaction
 (2) Zero order reaction
 (3) Second order reaction
 (4) Fractional order of reaction
- 83.** $2A \rightarrow \text{Product}$, follows the first order kinetics. If the half life period of the reaction at $[A]_{\text{initial}} = 0.2 \text{ mol L}^{-1}$ is 20 min. then the value of rate constant would be:-
 (1) 4 s^{-1} (2) 20 s^{-1}
 (3) $4 \text{ lit. mol}^{-1} \text{ min.}^{-1}$ (4) 0.034 min^{-1}
- 84.** Correct statement about first order reaction is:-
 (1) $t_{\text{completion}} = \text{finite}$
 (2) $t_{1/2} \propto \frac{1}{a}$
 (3) Unit of K is $\text{mole lit}^{-1} \text{ s}^{-1}$
 (4) $t_{1/2} \times K = \text{at constant temperature}$

COLLISION THEORY AND FACTORS AFFECTING RATE OF REACTION

- 85.** According to collision theory of reaction rates –
 (1) Every collision between reactants leads to chemical reaction
 (2) Rate of reaction is proportional to velocity of molecules
 (3) All reactions which occur in gaseous phase are zero order reaction
 (4) Rate of reaction is directly proportional to collision frequency.
- 86.** Activation energy of a reaction is –
 (1) The energy released during the reaction
 (2) The energy evolved when activated complex is formed
 (3) Minimum extra amount of energy needed to overcome the potential barrier of reaction
 (4) The energy needed to form one mole of the product
- 87.** The minimum energy for molecules to enter into chemical reaction is called.
 (1) Kinetic energy (2) Potential energy
 (3) Threshold energy (4) Activation energy
- 88.** The rate constant k_1 of a reaction is found to be double that of rate constant k_2 of another reaction. The relationship between corresponding activation energies of the two reactions at same temperature (E_1 & E_2) can be represented as
 (1) $E_1 > E_2$ (2) $E_1 < E_2$
 (3) $E_1 = E_2$ (4) $E_1 = 4E_2$



- 89.** At room temperature the reaction between NO and O_2 to give NO_2 is fast while that between CO and O_2 is slow it is due to –
 (1) CO is smaller in size than that of NO
 (2) CO is poisonous
 (3) The activation energy for the reaction $2NO + O_2 \rightarrow 2NO_2$ is less than $2CO + O_2 \rightarrow 2CO_2$
 (4) NO_2 is poisonous
- 90.** Chemical reaction occurs as a result of collision between reacting molecules. Therefore the reaction rate is given by
 (1) Total number of collisions occurring in a unit volume per second
 (2) Fraction of molecules which possess energy less than the threshold energy.
 (3) Total number of effective collisions
 (4) Temperature
- 91.** An endothermic reaction $A \rightarrow B$ have an activation energy 15 kCal/mol and the heat of the reaction is 5 k cal/mol. The activation energy of the reaction $B \rightarrow A$ is –
 (1) 20 kCal/mol (2) 15 kCal/mol
 (3) 10 kCal/mol (4) Zero
- 92.** A large increase in the rate of a reaction for a rise in temperature is due to –
 (1) Increase in the number of collisions
 (2) Increase in the number of activated molecules
 (3) Lowering of activation energy
 (4) Shortening of the mean free path
- 93.** Rate of which reactions increases with temperature
 (1) Of any reaction
 (2) Of exothermic reaction
 (3) Of endothermic reaction
 (4) Can't be predicted
- 94.** The rate of a chemical reaction doubles for every $10^\circ C$ rise in temperature. If the temp is increased by $60^\circ C$ the rate of reaction increases by :
 (1) 20 times (2) 32 times
 (3) 64 times (4) 128 times
- 95.** According to the arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of chemical reaction ($\log k$) against.
 (1) (T) (2) $\log T$
 (3) $\frac{1}{T}$ (4) $\log \frac{1}{T}$
- 96.** Which plot will give the value of activation energy.
 (1) k v/s T (2) $\frac{1}{k}$ v/s T
 (3) $\ln k$ v/s T (4) $\ln k$ v/s $\frac{1}{T}$
- 97.** Given that k is the rate constant for some order of any reaction at temp T then the value of $\lim_{T \rightarrow \infty} \log k$ _____.
 (1) $A/2.303$ (2) A
 (3) $2.303 A$ (4) $\log A$
- 98.** From the following data; the activation energy for the reaction (Cal/mol) $H_2 + I_2 \rightarrow 2HI$
- | T (in K) | $1/T$ (in K^{-1}) | $\log_{10} k$ |
|----------|----------------------|---------------|
| 769 | 1.3×10^{-3} | 2.9 |
| 667 | 1.5×10^{-3} | 1.1 |
- (1) 4×10^4 (2) 2×10^4
 (3) 8×10^4 (4) 3×10^4
- 99.** The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at $25^\circ C$ are $3 \times 10^{-4} s^{-1}$; $104.4 kJ mol^{-1}$ and $6.0 \times 10^{14} s^{-1}$ respectively, the value of the rate constant as $T \rightarrow \infty$ is.
 (1) $2 \times 10^8 s^{-1}$ (2) $6 \times 10^{14} s^{-1}$
 (3) Infinity (4) $3.6 \times 10^{30} s^{-1}$
- 100.** For an endothermic reaction where ΔH represents the enthalpy of the reaction in kJ/mol ; the minimum value for the energy of activation will be
 (1) Less than ΔH (2) Zero
 (3) More than ΔH (4) Equal to ΔH
- 101.** The rate of reaction increases to 2.3 times when the temperature is raised from 300 K to 310 K. If K is the rate constant at 300 K then the rate constant at 310 K will be equal to –
 (1) $2k$ (2) k
 (3) $2.3k$ (4) $3k^2$
- 102.** If concentration of reactants is increased by 'x' then the k becomes –
 (1) $\ln \frac{k}{x}$ (2) $\frac{k}{x}$
 (3) $k + x$ (4) k



103. If the concentration units are reduced by n times then the value of rate constant of first order will

- (1) Increases by n times
- (2) Decreases by factor of n
- (3) Remain constant
- (4) Decrease $1/n$ times

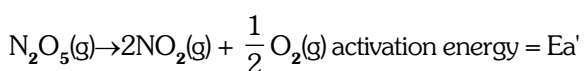
104. Which is used in the determination of reaction rates.

- (1) Reaction Temperature
- (2) Reaction Concentration
- (3) Specific rate constant
- (4) All of these

105. The rate constant of a first order reaction depends on the :-

- (1) Concentration of the reactant
- (2) Concentration of the product
- (3) Time
- (4) Temperature

106. For the decomposition of $N_2O_5(g)$ it is given that—
 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ activation energy = E_a



then

- (1) $E_a = 2E_a'$
- (2) $E_a > E_a'$
- (3) $E_a < E_a'$
- (4) $E_a = E_a'$

107. For a reaction in which case the activation energies of forward and reverse reactions are equal :-

- (1) $\Delta H = 0$
- (2) $\Delta S = 0$
- (3) The order is zero
- (4) There is no catalyst

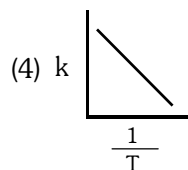
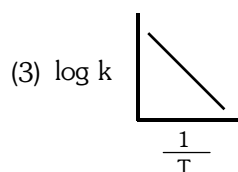
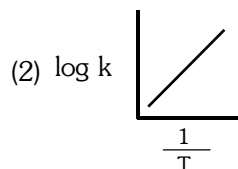
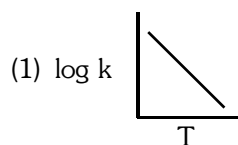
108. The energy of activation of a forward reaction is 50 kCal. The energy of activation of its backward reaction is:-

- (1) Equal to 50 kCal.
- (2) Greater than 50 kCal.
- (3) Less than 50 kCal.
- (4) Either greater or less than 50 kCal.

109. An exothermic reaction $X \rightarrow Y$ has an activation energy 30 kJ mol^{-1} . If energy change (ΔE) during the reaction is -20 kJ , then the activation energy for the reverse reaction is :-

- (1) 10 kJ
- (2) 20 kJ
- (3) 50 kJ
- (4) -30 kJ

110. Which of the following plot is in accordance with the arrhenius equation :-



111. The rate of reaction increases by the increase of temperature because :-

- (1) Collision is increased
- (2) Energy of products decreases
- (3) Fraction of molecules possessing energy $\geq E_T$ (Threshold energy) increases
- (4) Mechanism of a reaction is changed

112. For a certain gaseous reaction rise of temperature from 25°C to 35°C doubles the rate of reaction. What is the value of activation energy :-

(1) $\frac{10}{2.303R \times 298 \times 308}$

(2) $\frac{2.303 \times 10}{298 \times 308R}$

(3) $\frac{0.693R \times 10}{290 \times 308}$

(4) $\frac{0.693R \times 298 \times 308}{10}$



- 113.** The activation energy for the forward reaction $X \rightarrow Y$ is 60 kJ mol^{-1} and ΔH is -20 kJ mol^{-1} . The activation energy for the backward reaction $Y \rightarrow X$ is:-
 (1) 80 kJ mol^{-1} (2) 40 kJ mol^{-1}
 (3) 60 kJ mol^{-1} (4) 20 kJ mol^{-1}

- 114.** For producing the effective collisions, the colliding molecules must possess:-
 (1) A certain minimum amount of energy
 (2) Energy equal to or greater than threshold energy
 (3) Proper orientation
 (4) Threshold energy as well as proper orientation of collision

- 115.** The half life for a reaction is -----of temperature:-
 (1) Independent
 (2) Increased with increase
 (3) Decreased with increase
 (4) Increased or decreased with increase

- 116.** The activation energy for a chemical reaction depends upon :-
 (1) Temperature
 (2) Nature of reacting species
 (3) Concentration of the reacting species
 (4) Collision frequency

EXERCISE-I (Conceptual Questions)

ANSWER KEY

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ans. | 1 | 1 | 3 | 3 | 1 | 4 | 1 | 3 | 1 | 4 | 2 | 4 | 3 | 3 | 2 |
| Que. | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| Ans. | 3 | 2 | 2 | 2 | 1 | 3 | 3 | 2 | 2 | 4 | 3 | 3 | 2 | 2 | 3 |
| Que. | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 |
| Ans. | 4 | 2 | 2 | 3 | 2 | 1 | 2 | 4 | 1 | 3 | 2 | 1 | 3 | 4 | 3 |
| Que. | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | 55 | 56 | 57 | 58 | 59 | 60 |
| Ans. | 1 | 3 | 2 | 1 | 4 | 1 | 2 | 2 | 4 | 4 | 2 | 4 | 3 | 2 | 1 |
| Que. | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 |
| Ans. | 3 | 4 | 3 | 2 | 3 | 1 | 3 | 2 | 2 | 3 | 3 | 1 | 2 | 4 | 3 |
| Que. | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | 87 | 88 | 89 | 90 |
| Ans. | 1 | 2 | 2 | 4 | 2 | 1 | 2 | 4 | 4 | 4 | 3 | 3 | 2 | 3 | 3 |
| Que. | 91 | 92 | 93 | 94 | 95 | 96 | 97 | 98 | 99 | 100 | 101 | 102 | 103 | 104 | 105 |
| Ans. | 3 | 2 | 1 | 3 | 3 | 4 | 4 | 1 | 2 | 3 | 3 | 4 | 3 | 4 | 4 |
| Que. | 106 | 107 | 108 | 109 | 110 | 111 | 112 | 113 | 114 | 115 | 116 | | | | |
| Ans. | 4 | 1 | 4 | 3 | 3 | 3 | 4 | 1 | 4 | 3 | 2 | | | | |



EXERCISE-II (Assertion & Reason)

Directions for Assertion & Reason questions

These questions consist of two statements each, printed as Assertion and Reason. While answering these Questions you are required to choose any one of the following four responses.

- (A) If both Assertion & Reason are True & the Reason is a correct explanation of the Assertion.
(B) If both Assertion & Reason are True but Reason is not a correct explanation of the Assertion.
(C) If Assertion is True but the Reason is False.
(D) If both Assertion & Reason are false.

1. **Assertion** : The rate of the reaction is the rate of change of concentration of a reactant or a product.
Reason : Rate of reaction remains constant during the complete reaction.
(1) A (2) B (3) C (4) D
2. **Assertion** : The molecularity of a reaction is a whole number other than zero, but generally less than 3.
Reason : The order of a reaction is always whole number
(1) A (2) B (3) C (4) D
3. **Assertion** : Formation of HI is a bimolecular reaction.
Reason : Two molecules of reactants are involved in this reaction.
(1) A (2) B (3) C (4) D
4. **Assertion** : If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.
Reason : For a zero order reaction, the rate of reaction is independent of initial concentration.
(1) A (2) B (3) C (4) D
5. **Assertion :-** In a first order reaction the rate constant double on doubling the initial concentration of the reaction.
Reason :- The rate constant varies directly with the concentration of the reactants in a first order reaction.
(1) A (2) B (3) C (4) D
6. **Assertion :-** Rate of reaction double when concentration of reactant is double if it is a first order reaction.
Reason :- Rate constant also double.
(1) A (2) B (3) C (4) D
7. **Assertion** : For a first order reaction $t_{1/2}$ is independent of the initial concentration of reactants.
Reason : For a first order reaction $t_{1/2}$ is twice the $t_{3/4}$.
(1) A (2) B (3) C (4) D
8. **Assertion** : Acid catalysed of ethyl acetate is a first order reaction.
Reason : Water does not take part in the reaction.
(1) A (2) B (3) C (4) D
9. **Assertion** : Half life period is always independent of initial concentration.
Reason : Half life period is directly proportional to rate concentration.
(1) A (2) B (3) C (4) D
10. **Assertion** : In a reversible endothermic reaction activation energy of the forward reaction is higher than that of the backward reaction.
Reason : The threshold energy of the forward reaction is more than that of the backward reaction.
(1) A (2) B (3) C (4) D
11. **Assertion** : The reaction having low value of activation energy are generally fast.
Reason : Temperature coefficient for reaction having low activation energy is large.
(1) A (2) B (3) C (4) D
12. **Assertion :-** Two different reaction can never have same rate of reaction
Reason :- Rate of reaction always depends only on frequency of collision and Arrhenious factor
(1) A (2) B (3) C (4) D
13. **Assertion :-** Rate constant of reaction depends on concentration of reactant.
Reason :- On changing concentration, rate of reaction always increases.
(1) A (2) B (3) C (4) D



14. Assertion :- On increasing the temperature by 10°C , rate constant almost doubles.

Reason : On increasing temperature by 10°C , collision frequency doubles.

(1) A (2) B (3) C (4) D

15. Assertion :- On increasing temperature rate of reaction always increases.

Reason :- For any reaction equilibrium always shifts in forward direction on increasing temperature.

(1) A (2) B (3) C (4) D

16. Assertion : Catalyst increases rate of reversible reaction.

Reason : It increase the E_a for forward reaction but decreases the activation energy for backward reaction.

(1) A (2) B (3) C (4) D

EXERCISE-II (Assertion & Reason)

ANSWER KEY

| Que. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|------|----|---|---|---|---|---|---|---|---|----|----|----|----|----|----|
| Ans. | 3 | 3 | 1 | 2 | 4 | 3 | 3 | 3 | 4 | 3 | 3 | 4 | 4 | 3 | 3 |
| Que. | 16 | | | | | | | | | | | | | | |
| Ans. | 3 | | | | | | | | | | | | | | |

